INFLUENCE OF INTERATOMIC RESONANCE ON THE FREQUENCY OF RE-EMITTED RESONANCE RADIATION*

G. S. KASTHA

Optics Department, Indian Association for the Cultivation of Science, Calcutta-32

(*Received, November* 6, 1959)

ABSTRACT. The presence of radiations of changed frequencies, reported earlier, in the spectra of the resonance radiation of sodium and mercury filtered by the vapour of the corresponding element, has been explained on the hypothesis of resonance interactions between two excited atoms of the element. It has been pointed out that, according to this hypothesis, the maximum separation between the components of the transmitted doublet in the case of D_2 line of sodium would be twice that in the case of the D_1 line. This agrees fairly with the relative values of the maximum separation between the components of the doublets in these cases, reported previously.

INTRODUCTION

It was observed by Kastha (1949, 1953), that when almost monochromatic resonance radiation of sodium and mercury are filtered through vapours of the corresponding elements at different temperatures and pressures, the resonance lines are not fully absorbed by the vapours and the transmitted lines appear as weak doublets. It was also found that the separation between the intensity-maxima in the doublet in each case increases with increase in the pressure of the absorbing vapour and their intensity decreases rapidly with the increase in the separation. It was further observed that the separation between the two components of the doublet observed in the case of D_2 line of sodium was about one and half times that in the case of the D_1 line. It has been concluded, from these results, that fluorescence radiations of changed frequencies, not present in the incident radiations, are created during the process of absorption and re-emission of the absorbed radiations by atoms of the absorbing vapour at suitable pressures. It was pointed out that the change in the frequency observed in these cases are much larger than those due to Doppler effect and Van der Waals forces.

As a qualitative explanation of the change of frequency of the re-emitted resonance line it was suggested that the emission might have taken place at the instant of collision between the excited atom and another neighbouring atom. In the present paper, the problem has been examined from quantum mechanical point of view and attempt has been made to explain the observed change in the frequency of the transmitted lines in the different cases.

*Communicated by Prof. S. C. Sirkar.

INFLUENCE OF RESONANCE BETWEEN TWO NEIGHBOURING EXCITED ATOMS ON THE FREQUENCY OF EMITTED RADIATION

If a photon of proper frequency is incident on a system consisting of two atoms close to each other, one of the atoms may be excited through absorption of the radiation, but it is difficult to ascertain which of the two atoms is excited. Hence a resonance between the two atoms takes place. As a result, the energy level of the normally excited atom is slightly changed. The magnitude of this perturbation has been worked out by Margenau and Watson (1936) They have also shown that, due to variation in the distance of approach between the two interacting atoms, the perturbed energy states of the system containing the two atoms, instead of being descrete, are broadened symmetrically about its unperturbed position If now continuous radiation is incident on the system consisting of such a pair of atoms the absorption of radiations by the pair would take place at frequencies slightly different from the frequency corresponding to the normal excited energy level of the atom.

In the present case, however, only the resonance radiation of definite frequency was incident on the atoms of the absorbing vapour, and therefore, any pair of atoms in resonance could not be excited by this radiation The isolated atoms, however, could absorb the radiation and pass on to the excited state. We can postulate the following process of emission by the excited atoms, in which a change in the wavelength of the emitted radiation can be produced by the influence of the neighbouring atoms on each other.

Let us consider two such atoms 1 and 2, excited by absorption of resonance radiation incident on them while they were sufficiently apart from each other, and also, that at a certain instant before one of the two atoms is about to radiate, they come sufficiently close enough. Such an assumption is justified, as would be evident from the following considerations

Corresponding to the pressure of the absorbing mercury vapour at 373°K, the number of atoms per c.c. is about 7.10^{15}, and consequently, the average distance between two atoms of mercury is of the order of 500 A.U. Since the average velocity of mercury atom at this temperature is about 3.10^4 cm/sec., the time required for two excited atoms separated by this distance to come close together is about 10^{-10} sec., which is small compared to the life time of 10^{-7} sec. of the excited state of the mercury atom (Garrett, 1932). Similarly, in the case of sodium vapour at about 560°K, the average distance between two neighbouring atoms is about 1000 A.U., and as the average velocity of the sodium atom at this temperature is about 10^5 cm/sec, the time required for two excited atoms of sodium separated originally by this distance to come closer together is about 10^{-10}sec. This is small compared to the life time of the excited state which is about 10^{-8} sec (Minkowski, 1926).

If we consider that the two excited atoms form a system, the system may be described by the composite wavefunction $\psi'(1)\psi'(2)$, where $\psi'(1)$ and $\psi'(2)$ are the excited state wave functions of the isolated excited atoms 1 and 2 respectively. There are two possibilities by which the system can return to the unexcited state. Either, both the atoms may radiate simultaneously or, they can do so one after another. Since the probability of the first process is small, we shall consider the second process only. In this case, an intermediate state of the system may be represented by either of the two following wave functions (Margenau and Watson 1936),

$$\psi' = \frac{1}{\sqrt{2}} [\psi(1)\psi'(2) + \psi'(1)\psi(2)]$$

$$\psi'' = \frac{1}{\sqrt{2}} [\psi(1)\psi'(2) - \psi'(1)\psi(2)]$$

while the final state can be written simply as $\psi(1)\psi(2)$. The linear combination of terms like $\psi(1)\psi'(2)$ takes account of the fact that either of the atoms may finally be in the unexcited state represented by ψ-function without prime. As pointed out by Margenau and Watson (1936), since the radiation from the initial state to the intermediate state and also from this state to the final state takes place through electric dipole radiation, the state given by ψ'' is excluded, for the transition moments due to transition to and from this state vanish. The energy of the initial state of the system, given by $\psi'(1)\psi'(2)$, will be $2E_0$, where E_0 is the energy of the normally excited atom, but the intermediate state will have a perturbation energy besides E_0. The change in the energy was calculated by Margenau and Watson (1936) and is given by

$$\Delta\epsilon = -\frac{2}{3}\frac{e^2}{R^3}|r_{12}|^2 \quad \text{for} \quad m = 0$$

and

$$\Delta\epsilon = +\frac{1}{3}\frac{e^2}{R^3}|r_{12}|^2 \quad \text{for} \quad m = \pm 1$$

where R is the distance between the two atoms 1 and 2 and the m's refer to the magnetic quantum number of the excited state, $|r_{12}|^2$ is given by $|r_{12}|^2 = \frac{3hf\lambda}{8\pi^2 cm_e}$, where $|r_{12}|$ denotes the linear transition moment, m_e the electronic mass, λ the wave length of the resonance radiation, f the oscillator strength connected with this radiation and the other quantities have usual significance.

The energy of the radiated quantum will thus be $2E_0-(E_0+\Delta\epsilon) = E_0-\Delta\epsilon$, where $\Delta\epsilon$ has one of the values indicated above. From this intermediate state the system can return to the ground state with the emission of a further quantum

with an energy of $E_0+\Delta\epsilon$, slightly different from E_0, as shown in figure 1. Thus the maximum frequency-shift on either side of the centre of the resonance radiation, would be $\frac{\Delta\epsilon}{hc} = \frac{e^2 f\lambda}{4\pi^2 c^2 R^3 m_e}$ cm^{-1} Since the value of $\Delta\epsilon$ depends on R, the radiated energies of changed frequencies would not be descrete but would have

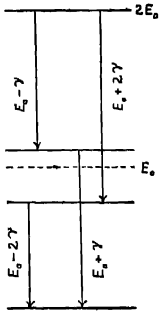

Fig. 1. Schematic energy levels of a pair of atoms in resonance.

a continuous nature, for R may have all possible values. It is also evident that those events, in which R will have a small value, will be rare compared to those in which the value of R is large, and accordingly, the intensity of radiations with relatively large frequency shifts will also be small. Moreover, as the probability of the excited atoms coming closer increases with the increase of temperature and pressure of the absorbing vapour, the extent by which the frequency of the emitted radiation changes also increases. It might, however, be mentioned that the probability of occurrence of the second process would depend on the availability of a large number of excited atoms, and therefore, the following conditions should be fulfilled:

(1) The f-value, i.e. the oscillator strength of the resonance radiation of the element concerned must be large, and

(2) the number of atoms per c.c. of the given element at a given temperature should be sufficiently high.

It is seen that $\Delta\epsilon$ varies directly as the value of the oscillator strength and therefore, the value of $\Delta\epsilon$ for D_1 and D_2 lines of sodium should be different. The values of f for D_1 and D_2 lines are 0.333 and 0.667 respectively, and so the value of $\Delta\epsilon$ for D_2 is expected to be double that for D_1. It is interesting to note, as was previously reported (Kastha, 1953), that actually the separations for D_2 and D_1 are in the ratio 3 : 2. This is in fair agreement with the explanation given above.

All the radiated energies of changed wavelengths would not be transmitted by the vapour of the absorbing element, but a part of it would be absorbed due to resonance broadening of the absorption level of pairs of neighbouring atoms of the element

If we put $\gamma = e^2hf\lambda/8\pi^2R^3cm_e$, the energy of the radiation emitted, during transition from the initially excited state to the intermediate state, is either $E_0+2\gamma$ or $E_0-\gamma$, as can be seen from figure 1. Further, transition from this latter state to the unexcited final state creates radiations of energy equal to either $E_0+\gamma$ or $E_0-2\gamma$. Hence, the radiations due to the former transition can not be absorbed by a pair of atoms in resonance and separated by the same distance R as in the case of emission, although there is some probability of absorption of the radiations due to transition from the intermediate state to the ground state. Even in the latter case, some fraction of the total intensity will escape. Hence, the maximum separation between the components of the transmitted radiations is expected to be $4\gamma/hc$ cm^{-1}. If the observation is made in a particular direction, while the radiation takes place in all directions, the intensity is expected to be small and this may be another reason for the observed weakness of the doublets.

It would be interesting to calculate the distance of closest approach between two atoms of sodium and between two atoms of mercury in the respective vapour from the magnitude of the separations between the components of the transmitted doublets observed in these cases (Kastha, 1949, 1953)

The value of R is calculated with the help of the following two formulae,

$$\Delta\nu(\text{cm}^{-1}) = \frac{2}{3}\frac{e^2}{chR^3}|r_{12}|^2$$

and

$$|r_{12}|^2 = \frac{3hf\lambda}{8\pi^2cm_e}.$$

The values of all the quantities used are in C. G. S. units The calculated values of R, together with other relevant data, are given in Table I

TABLE I

Element	Wavelength of the Resonance Radiation in A.U.	Oscillator Strength f	$\Delta\nu$ in cm^{-1}	Distance R in A.U.
Na	5895.9(D_1)	1/3	1.125	50
	5889.9(D_2)	2/3	1.575	56
Hg	2536.6	1/35	9.3	8.2

It is seen from the above table that the value of R in the case of mercury is much smaller than that observed with sodium. Though the vapour pressure of mercury (.273 mm) at 373°K is much larger than that of sodium at 563°K (9.1×10^{-3} mm), this alone may not be sufficient to explain the small value of R obtained in the former case. However, in the investigation with resonance radiation of mercury, the absorption cell through which the radiation was filtered contained nitrogen at a pressure of about one atmosphere (Kastha, 1949), and the small value of R may be due to local inhomogeneity in the distribution of atoms in the mixture.

ACKNOWLEDGMENT

The author's thanks are due to Prof. S. C. Sirkar, D.Sc., F.N.I., for his kind interest and valuable discussions and also to Prof. D. Basu, Ph.D., for helpful suggestions

REFERENCES

Garrett, P. H., 1932, *Phys. Rev.*, **40**, 779.
Kastha, G. S., 1949, *Ind. J. Phys.*, **23**, 247.
,, 1953, *Ind. J. Phys.*, **27**, 67.
Margenau, H. and Watson., W. W., 1936, *Rev. Mod. Phys.*, **8**, 22.
Minkowski, R., 1926, *Z. f Phys.*, **36**, 839.